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MoS₂ decoration by Mo-atoms and the MoS₂– Mo–graphene heterostructure: a theoretical study

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Here we propose a completely new covalent heterostructure based on graphene and self-decorated MoS₂ monolayers. Detailed investigation of the decoration process of the MoS₂ surface by Mo adatoms was performed using first principles DFT methods. Comparison between valence-only and semicore pseudopotentials was performed to correctly describe the interaction between Mo adatoms and the MoS₂ surface. It was found that self-decoration by Mo atoms is favorable from an energetic point of view. We studied in detail various decoration paths of Mo atoms on the MoS₂ surface. The strong variation of electronic properties after the decoration of MoS₂ was found. The impact of the presence of Mo adatoms on the electronic properties of the graphene/MoS₂ heterostructure was shown.

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Introduction

The developing field of two-dimensional materials reached the stage of investigation of complex nanostructures based on already known 2D films. The available experimental data hold promise for establishing a completely new scientific field of artificial quasi-two-dimensional heterostructures with properties being dependent on constituted 2D layers.^{1–4} This perspective attracts significant attention for the investigation of the surface of the 2D nanostructures, especially for their interaction with additional atoms which is highly important for the creation of an atomically sharp interface between neighboring films in the heterostructure. The surface properties of transition metal dichalcogenides are most important because atomic films of such composition are usually part of a new generation of 2D heterostructures due to their semiconducting properties and chemical robustness.⁵ Nevertheless the additional atom adsorption can lead to a substantial change of the film properties. For example, the adsorption of Li atoms on MoS₂ or WS₂ can lead to the transition of the semiconducting 2H phase to the metallic 1T phase.^{6–9} Partial transformation and coexistence of two phases by structural stabilization through substitutional doping¹⁰ or adsorption of metal atoms on the TMD's surface¹¹ may be a valuable method to achieve metal-semiconductor hybrid structures.

Moreover Lin *et al.*¹² demonstrated the doping (deposition) with Re and Au atoms on single layer MoS₂ using a chemical vapor transport (CVT) technique and also it was shown experimentally in

consistence with DFT calculations that adsorbed Re enhances the local chemical affinity, evidenced by the agglomeration of other dopant/impurity atoms. Motivated by these results we suggest here the formation of layered heterostructures connected with each other by adsorbed metal atoms. From the wide variety of possible metals we have chosen molybdenum itself in terms of homo-adsorption. Molybdenum can for example be deposited on MoS₂ by an atomic layer deposition (ALD) process.¹³

Intermediate metal links could change the interaction inside the heterostructure from van der Waals to covalent, tune the electronic properties and increase the mechanical characteristics associated with shear deformations.

Results and discussion

Here we focused on the investigation of interaction between graphene and the MoS₂ surface through Mo adatoms which were adsorbed directly on the MoS₂ surface. Surprisingly we discovered that despite the inertness of the MoS₂ surface the decoration process of Mo adatoms is energetically favorable, whereas the small value of the estimated migration barrier hints at the high mobility of Mo atoms on the surface. This result allows the conclusion that the MoS₂ surface can be decorated by individual Mo adatoms which can substantially change the electronic and chemical properties of the layer. Finally, we investigated the properties of double-layer heterostructure graphene/MoS₂ with Mo atoms attached to the MoS₂ surface and found out that the adatoms may form bonds between layers and introduce new states near Fermi energy which may create conduction channels.

All calculations in this paper are based on first-principles calculations within density functional theory (DFT) using the

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projected augmented waves method (PAW) implemented in VASP package^{14,15} using periodic boundary conditions within a supercell geometry. General gradient approximation of the Perdew–Burke–Ernzerhof¹⁶ parameterization was applied. The plane-wave cutoff and Brillouin zone sampling were determined after test calculations. To avoid the interaction between periodic images the large spacing ~ 10 Å was used in nonperiodic directions – perpendicular to the layer. The cutoff energy for the plane-wave basis set was set to be 400 eV. To calculate equilibrium atomic structures, the Brillouin zone was sampled according to the Monkhorst–Pack scheme with a $6 \times 6 \times 1$ k -point set for a 4×4 supercell of MoS₂. Structural relaxation was performed until the forces acting on each atom became less than 0.05 eV Å⁻¹.

Valence-only pseudopotential (4d⁵5s¹) and semicore pseudopotential (4p⁶4d⁵5s¹) for Mo atoms were used for the description of interaction between the adatom and the MoS₂ surface. Both GGA and LDA approaches taking into account spin polarization were applied for test calculations. The formation energy of the MoS₂ layer and the binding energy of the Mo adatom were calculated using both types of pseudopotentials. The formation energy per MoS₂ unit was calculated by

$$E_f = E_{\text{tot}} - mE_{\text{Mo}} - nE_{\text{S}},$$

where E_{tot} , E_{Mo} , and E_{S} are the total energies of the MoS₂ unit cell, and of the ground state of isolated Mo and isolated S atoms, respectively. The total energies of isolated atoms were obtained using the same unit box as in the case of 4×4 MoS₂ supercell calculations. The formation energy of the MoS₂ layer was obtained as -22.32 eV per MoS₂ and -22.07 eV per MoS₂ for LDA and -16.33 eV per MoS₂ and -14.53 eV per MoS₂ for GGA with valence-only and semicore pseudopotentials, respectively. The difference between the formation energy values is caused only by the ground state energy of the isolated Mo atom. The total energy of the ground state calculated with GGA in the case of semicore pseudopotentials is 1.5 eV lower than that in the case of a valence-only one. LDA underestimates the ground state energy of the isolated Mo atom and overestimates the formation energy, respectively. The binding energy of Mo adatoms depends also on the type of Mo pseudopotential. All further calculations were carried out with the GGA semicore pseudopotential due to the good agreement of the formation energy with reference data.¹⁷

Calculations of the partial density of states of heterostructures based on graphene and decorated MoS₂ were carried out using a localized orbital method implemented in the SIESTA package.¹⁸ The exchange–correlation energy was approximated by the LDA.¹⁹ The plane-wave mesh cutoff was defined as 250 Ry. The band structures were calculated along Γ – M – K – Γ directions using 50 k -points in each direction.

We studied in detail the decoration process of the MoS₂ surface by Mo adatoms (self-decoration). Two possible binding sites of Mo adatoms on the MoS₂ surface were considered. These sites are defined by the different positions of the Mo adatoms with respect to the atoms in the layer, depicted in Fig. 1a, namely

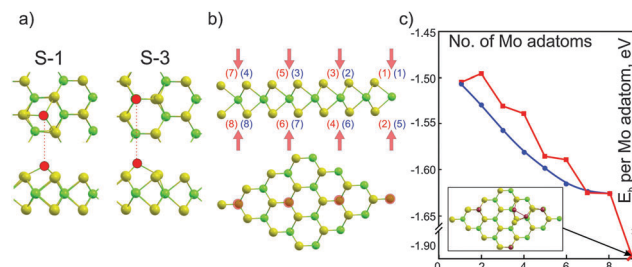


Fig. 1 (a) Atomic structure of MoS₂ with Mo adatoms in S-1 and S-3 sites. (b) Schematic representation of symmetric and asymmetric decoration paths (red and blue numbers correspond to the sequence of adsorption in symmetric and asymmetric paths, respectively). (c) Dependence of the binding energy per Mo adatom on the number of Mo adatoms on the surface. Red circles depict Mo adatoms onto the MoS₂ surface. In the inset the atomic structure of the MoS₂ surface with 9th Mo adatoms in the supercell is shown. Dark red circles depict the Mo adatoms.

S-1 and S-3. The decoration process of individual Mo atoms was studied on the surface of the 4×4 MoS₂ supercell.

The binding energy as a function of the decoration was calculated as:

$$E_b = E_{\text{tot}} - E_{\text{MoS}_2} - E_{\text{atom}}$$

where E_{tot} , E_{Mo} , and E_{S} are the total energies of the MoS₂ layer with an additional Mo atom, and a pure MoS₂ layer and the energy of an isolated Mo atom, respectively. The binding energy between the Mo adatom and the MoS₂ surface was determined as -1.23 eV and -1.51 eV for S-1 and S-3 sites, respectively. The energetically favorable location of a Mo atom at a S-3 site (on top of a Mo atom in the layer) allows us to consider the further study only for this site. The decoration process was performed atom by atom onto the surface of the supercell in two paths: an asymmetric path, when adatoms firstly cover the upper side and then the lower side of the surface (blue numbers in Fig. 1b) and a symmetric path in which adatoms are placed alternately on both surfaces (red numbers in Fig. 1b). The distance between the adatoms was chosen to be more than 4 Å to avoid the interaction between neighboring adatoms on the surface. In Fig. 1b the comparison between the binding energies per Mo adatom for both paths of decoration is presented. We found out that the energetically preferred decoration is the asymmetric one – when adatoms firstly cover one side of the film and chemically activate the other side for binding. In this case the binding energy monotonically increases in absolute value with the increasing number of Mo adatoms. Whereas in the case of the symmetric path (red color) the increase of the number of adatoms leads to a step-like increase (in absolute value) of the binding energy.

After the uniform coverage of both MoS₂ surfaces both paths yield the same binding energy (eighth step at Fig. 1c). Further adsorption of the Mo adatom on the MoS₂ surface leads to the formation of Mo₂ clusters on the surface (see the inset of Fig. 1c). During this process the binding energy strongly decreases down to -1.94 eV, which is possible due to the reconstruction of the surface and the formation of the Mo

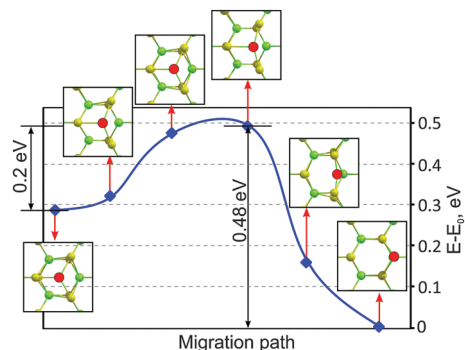


Fig. 2 The migration barrier of Mo adatoms on the MoS₂ surface from the S-1 to S-3 site. Red circles depict the adatoms.

clusters by the increase of the distance between Mo₂ and MoS₂ up to ~ 2.8 Å.

The possible formation of Mo₂ dimers requires an analysis of the migration barrier of adatoms on the MoS₂ surface. The migration from S-1 to S-3 sites was studied (Fig. 2). It was found that the energy barrier from the S-3 site (energy favorable) to the S-1 site is ~ 0.48 eV per unit cell, whereas the reverse energy barrier from S-1 to S-3 is only 0.20 eV per unit cell, which could possibly be overcome at room temperature.

Taking into account the low migration barriers it is possible to conclude that a MoS₂ surface can be covered only by scarcely distributed Mo adatoms without cluster formation. Besides the change in binding energy Mo adatoms strongly impact the electronic properties of the MoS₂ surface. The evolution of electronic properties at each step of decoration was investigated (Fig. 3). Adsorption of even the first Mo adatom (Fig. 3) leads to a strong decrease of the band gap (from 1.8 eV to 0.8 eV) with the formation of several additional impurity levels in the valence band.

In Fig. 4 the electronic densities of states for all steps of decoration are shown. Red and blue colors correspond to the

symmetric and asymmetric decoration paths, respectively. In the inset of Fig. 4 the decoration paths are sketched. Further decoration leads to the increase of the contribution of impurity levels in the valence band and a slow decrease of the band gap. After the adsorption of the 5th Mo adatom only a small difference between the symmetric and asymmetric paths is observed. Finally at the maximal number of Mo adatoms (8 atoms) the band gap is decreased down to 0.4 eV from 1.6 eV (pure MoS₂).

After the detailed study of the decoration process onto a MoS₂ surface and the impact on electronic properties the investigation of the layered structure based on graphene and decorated MoS₂ (covalent heterostructure) was carried out. We considered a hexagonal supercell consisting of (4×4) MoS₂ and (5×5) graphene unit cells with Mo adatoms between the layers. In Fig. 4 the detailed analysis of the electronic properties of a covalent heterostructure is presented. Mo adatoms formed covalent bonds with a graphene surface as well as with a MoS₂ surface which strongly changes the electronic structure (Fig. 4b).

The Mo adatoms play the role of a connecting link between graphene and MoS₂. Partial DOS for d orbitals of an additional Mo atom in the heterostructure, band structure and partial DOS for the heterostructure with Mo atoms between the layers is presented in Fig. 4. To estimate the contribution from each type of orbital of additional Mo atoms between the layers of MoS₂ and graphene the wave function of selected energy levels is also shown in Fig. 4. The Mo atoms between the layers introduce the new states with the energy close to the E_F (Fig. 4b). Detailed analysis of PDOS of the considered heterostructure shows that the d_{z²} orbitals of additional Mo atoms are responsible for the connection between the graphene and the MoS₂ surface (green line in Fig. 4a). Moreover d_{z²} orbitals play a major role in the formation of a link between the layers in the heterostructure.

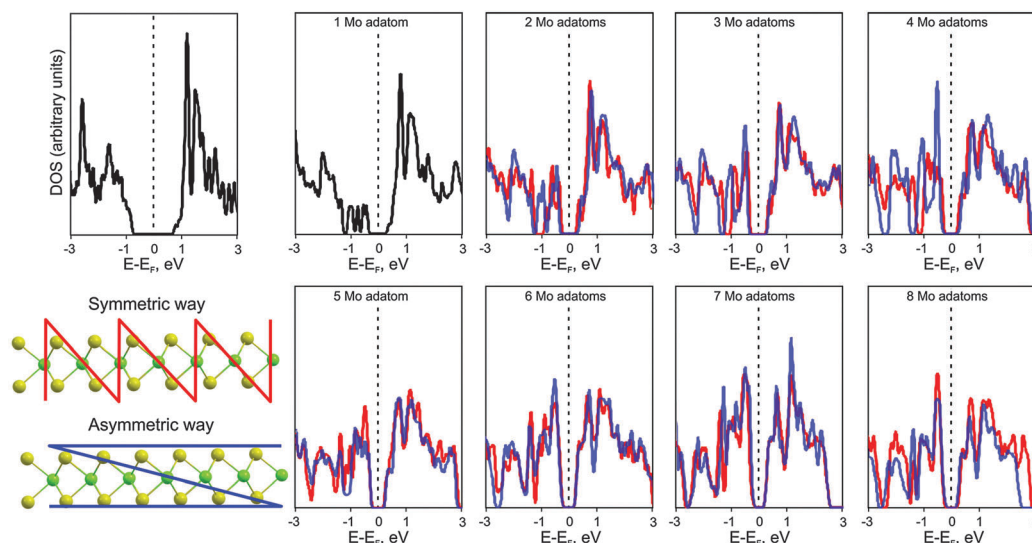


Fig. 3 Evolution of the electronic properties of the MoS₂ supercell decorated by 1–8 Mo adatoms. Schematic representation of the type of decoration path shown on the left. Red and blue colors correspond to the symmetric and asymmetric decoration paths, respectively.

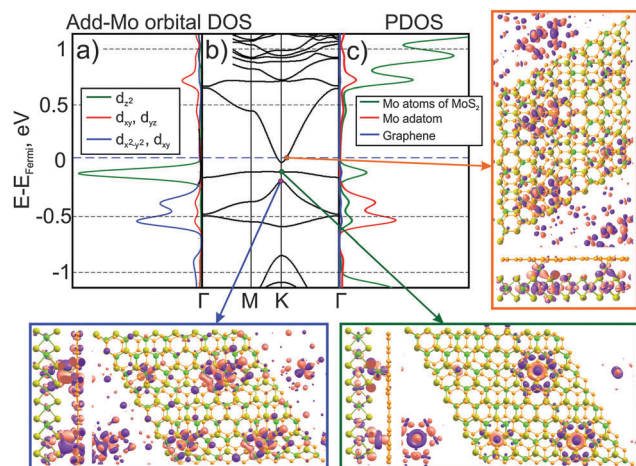


Fig. 4 (a) Orbital DOS of the covalent heterostructure based on graphene and decorated MoS_2 layers; (b) band structure; (c) partial DOS of the covalent heterostructure. Green, red and blue colors show the PDOS of Mo atoms in the layer, Mo adatom and graphene, respectively. The insets illustrate the wave function at energy levels indicated by circles in the band structure diagram.

Conclusions

A detailed theoretical study of the decoration process of the MoS_2 surface by Mo adatoms was performed. Comparison between the energies of two possible binding sites displays different behavior upon changing the adatom concentration. We found that self-decoration is preferred from the energetic point of view. Two various decoration paths named symmetric and asymmetric were studied. A strong increase of binding energy during the decoration was observed for both decoration types. The strong variation of electronic properties after the decoration of MoS_2 was observed. The impact of the presence of Mo adatoms on the graphene/ MoS_2 heterostructure electronic properties was also shown. It was found that the presence of Mo adatoms between the layers increases the interaction and conductive channels between graphene and MoS_2 are formed.

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